

# Characterization of Cationic Polyacrylamide-Grafted Starch Flocculant Synthesized by One-Step Reaction

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**ABSTRACT:** Cationic polyacrylamide-grafted starch (St-g-CPAM) flocculant was prepared by using corn starch and acrylamide (AM) as monomers, dimethyl diallyl ammonium chloride (DMDAAC) as cationic monomer through solution polymerization. The effects of initiator, reaction temperature, and monomer concentration on flocculation, the efficiency of grafting, and the yield of grafting were investigated. The results show that the optimal conditions of the polymerization are as follows: the concentration of ceric ammonium nitrate is 0.5%, the reaction temperature

is 60°C, the concentration of total monomer is 20%, and the monomer ratio between AM and DMDAAC is 7 : 3. The flocculation capability was characterized by turbidity reduction. The thermal behavior, chemical structure, and microstructure of St-g-CPAM were also investigated by thermal gravimetric, IR, and SEM analyses. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1261–1266, 2012

**Key words:** starch; graft; DMDAAC; (poly)acrylamide; flocculant

## INTRODUCTION

Wastewater discharge has become one of the most urgent problems for environmental protection. Flocculants are often used in fast solid–liquid separations by an aggregation process of colloidal particles. The process is termed as flocculation,<sup>1</sup> which has been widely used as an effective water treatment technology.<sup>2</sup> Flocculants can be classified into three groups: inorganic flocculants such as alum, ferrite flocculants or polyaluminum chloride; occurring flocculants, such as sodium alginate or microbial flocculants; and synthetic organic flocculants, such as polyacrylamide derivatives.<sup>3</sup> Among these flocculants, the use of alum usually leads to the problem of residual aluminum.<sup>4,5</sup> Ferrite flocculants can be costly, and the resultant excess iron may cause unpleasant metallic taste, odor, color, corrosion, foaming, or staining.<sup>3</sup> Although the synthetic organic flocculants are most frequently used because of the cost-effectiveness, they cause environmental pro-

blems that they are not readily biodegradable and some of their degraded monomers such as acrylamides (AMs) are neurotoxic and even show strong human carcinogenic potential.<sup>6</sup> To solve these problems, substitutes of natural polymers, such as starch, chitosan, cellulose, and so on have been investigated as an attractive alternative because natural polymers and their derivatives are biodegradable as well as their degradation intermediates are harmless to human beings and environment.

Starch is one of the most abundant natural polymers in the world, and as an important derivative of starch, cationic polyacrylamide-grafted starch (St-g-CPAM) has been widely used in many fields such as paper making, spinning, petroleum well drilling, medicine, daily chemicals, and floatation.<sup>7–9</sup> The conventional two-step method is first grafting AM to starch, and then adding formaldehyde and dimethylamine through Mannich reaction, which is complicated and not environmental friendly.<sup>7–9</sup> We previously synthesized polyacrylamide cationic flocculant with dimethyl diallyl ammonium chloride (DMDAAC) as cationic monomer, which has strong flocculation capability.<sup>10</sup> In this article, the starch was introduced into the flocculant because of its biodegradable property and relatively low price. St-g-CPAM was prepared by one-step reaction with DMDAAC as cationic monomer, which can avoid the toxicity of the formaldehyde. This one-step method of synthesizing St-g-CPAM, which has

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not been reported so far is easy to operate and hence has good commercial potentials.

## EXPERIMENTAL

### Materials

Corn starch was obtained from Simeite Food, China. AM was purchased from Fuchen Chemicals (Tianjin, China). DMDAAC, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), acetone, acetic acid glycol, and sodium hydroxide were supplied by Beijing Chemical Plant (China). Kaolin was purchased from Sanhe Kaolin, China. Formaldehyde, ammonium persulfate, azo initiator amidine, and ceric ammonium nitrate were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Deionized water was used throughout the experiments.

### Sample preparation

The reaction was carried out in a 250-mL four-necked round-bottom flask equipped with a stirrer, a thermometer, a condenser, and nitrogen gas inlet. The flask was heated in a thermostatic water bath. Corn starch (10 g) and 50-mL deionized water was poured into the flask and preheated for 30 min at 85°C. After the starch was gelatinized (starch slurry turned to a transparent solution), the flask contents were cooled to 40°C. Then, 14 g AM, 7 g DMDAAC, and 0.4 g ceric ammonium nitrate were added, and the mixture was allowed to react for 3 h at 55°C under N<sub>2</sub> protection. The product was washed with 200 mL acetone after dried and crushed. The crude product was obtained. Then, the crude product was washed three times with the solution of glacial acetic acid and ethylene glycol with a ratio of 40 : 60. The refined final product was obtained. The synthetic pathway is shown in Scheme 1.

### PG and GE properties

The percentage of grafting (PG) and the grafting efficiency (GE), and they can be calculated by the following formula:

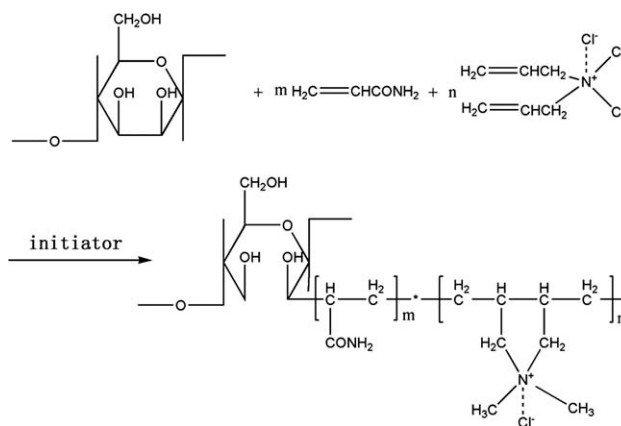
$$PG = [(M_2 - M_0)/M_0] \times 100\%$$

$$GE = (M_2/M_1) \times 100\%$$

where  $M_0$  is the weight of the starch,  $M_1$  is the weight of crude product, and  $M_2$  is the weight of refined product.

### FTIR analysis

The chemical structure of the St-g-CPAM flocculant surface was characterized by KBr disc method with



**Scheme 1** The synthetic pathway of St-g-CPAM.

a Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Nexus 670).

### TG analysis

The thermal stability of the St-g-CPMA flocculant was measured on a HCT-1 thermal gravimetric (TG) analyzer (Henjiu Scientific Instrument, Beijing) with a sample mass range of 5–10 mg and a heating rate of 10°C min<sup>-1</sup> under nitrogen protection.

### SEM analysis

Scanning electron microscopy (SEM) was conducted on a HITACHI S4700 instrument at room temperature to investigate the surface morphology of the St-g-CPAM flocculant samples. All the samples were sputtered with platinum before SEM analysis.

### Flocculation properties

Kaolin (1%) water solution was stirred for 4 h to form a suspension, followed by 24 h of settling time. The sample (1–2 mg) was put into 1000 mL of the kaolin solution and mixed them by stirring at the speed of 200 r min<sup>-1</sup>. The upper clear liquid was separated for further test. The turbidity of the upper clear solution of Kaolin was measured by WZT-3A photoelectric turbidimeter (Shanghai Scientific Instrument). The turbidity reduction can be calculated by the following formula:

$$\text{Turbidity reduction} = (N_0 - N_i)/N_0 \times 100\%$$

where  $N_0$  is the turbidity of the Kaolin solution,  $N_i$  is the turbidity of Kaolin solution which was treated with flocculant.

## RESULTS AND DISCUSSION

### PG and GE properties

Table 1 shows the effect of ceric ammonium nitrate concentration on grafting reaction. The reaction has

**TABLE I**  
The Effect of Ceric Ammonium Nitrate Concentration on Grafting Reaction

Concentration of ceric ammonium nitrate (%)	PG (%)	GE (%)
0.2	0	0
0.3	80.8	99.2
0.4	86.7	99.5
0.5	89.9	99.9

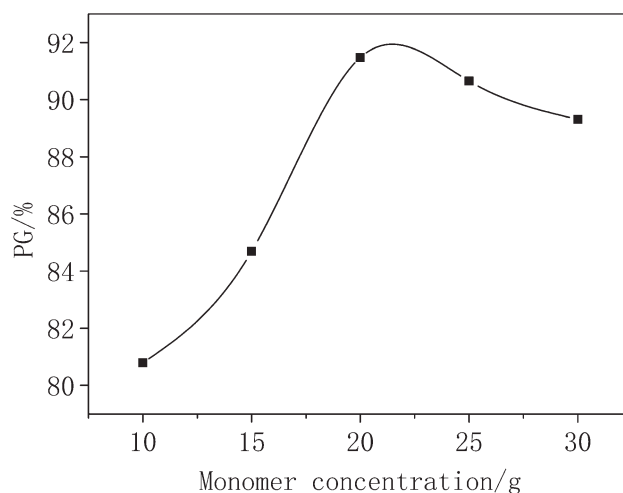
not been observed when the ceric ammonium nitrate is 0.2%. It is suggested the radical initiator is locked inside a cage when it is very less, which may cause side reaction and consume the initiator. This phenomenon is called "cage effect." When the initiator increases, the radical initiator is sufficient enough to come out from the cage to initiate the grafting process, and therefore, PG and GE increase with the initiator. When the ceric ammonium nitrate is 0.5%, the grafting reaction reaches its maximal point with PG and GE values of 89.9 and 99.9%, respectively.

Table 2 shows that PG and GE first increase and then decrease with reaction temperature. It is suggested the thermal motion of the molecules increases with the increase of the temperature, and more free radicals will be formed, and hence, the chain growth will be accelerated, resulting a higher PG. But when the temperature exceeds 60°C, molecular chains of St-g-CPAM may be broken, the chain transfer and chain termination of the reaction and polymerization rate also increase, which causes a obvious drop of GE at 65°C. So 60°C has been regarded as the optimal reaction temperature and has been used in following discussion.

Figures 1 and 2 show the effect of monomer concentration on grafting. It shows that PG and GE increase with the monomer concentration when it is less than 20%; however, they all show decreasing trends when the monomer concentration is more than 20%. The average number of free radicals increases with the monomer concentration which can increase them. However, when the total monomer mass increases to a certain value, the polymerization rate is accelerated and the residue monomer of AM increases, which can result the decrease of PG and GE. The high-

**TABLE II**  
The Effect of Reaction Temperature on Grafting

T (°C)	PG (%)	GE (%)
45	79.2	96.3
50	80.8	97.4
55	84.6	99.2
60	85.4	99.1
65	85.3	97.7



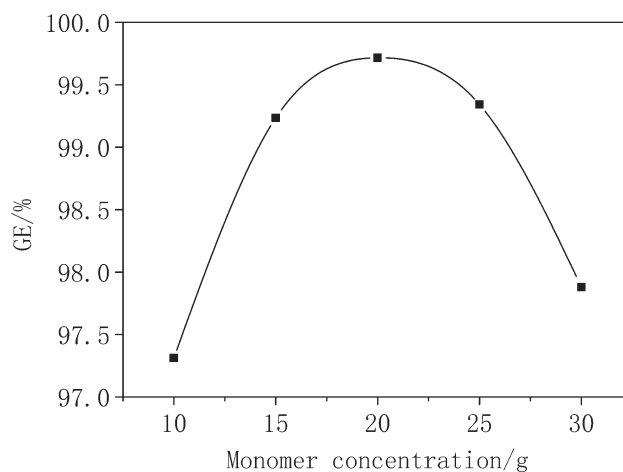
**Figure 1** The effect of monomer concentration on PG.

est value of PG and GE appear at the total mass of monomer concentration 20%.

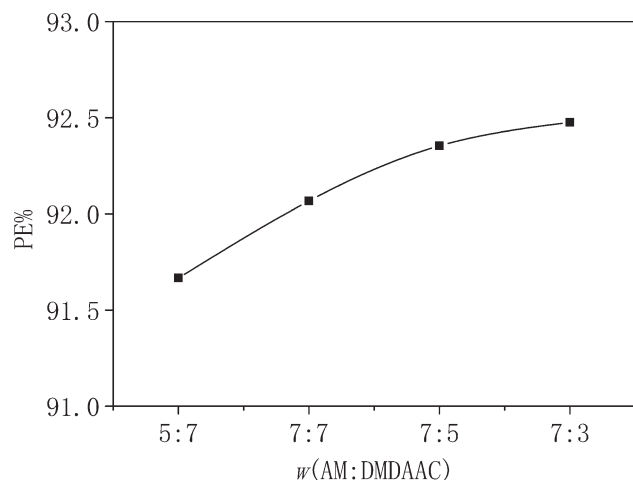
Figures 3 and 4 show that PG and GE increase with the amount of AM. The reactivity of AM is much higher than DMDAAC, therefore, the higher is the content of AM, the higher PG and GE are. But the cationic degree will decrease with the amount of AM. PG and GE reach their highest values at the AM : DMDAAC ratio of 7 : 3.

### FTIR analysis

The FTIR spectra of St-g-CPAM are shown in Figure 5. The broad band at 774  $\text{cm}^{-1}$  is due to the stretching mode of the glucose ring. The intense and broad peak at 1024 ~ 1052  $\text{cm}^{-1}$  is assigned to glucose ring of C—O stretching. Two peaks at 1404 and 2922  $\text{cm}^{-1}$  are corresponding to the characteristic absorption of C—C and —CH<sub>2</sub>—, respectively. The peak at 3428.8  $\text{cm}^{-1}$  is due to —NH<sub>2</sub>— stretching vibration. The peak of 1123–1452  $\text{cm}^{-1}$  is attributed



**Figure 2** The effect of monomer concentration on GE.

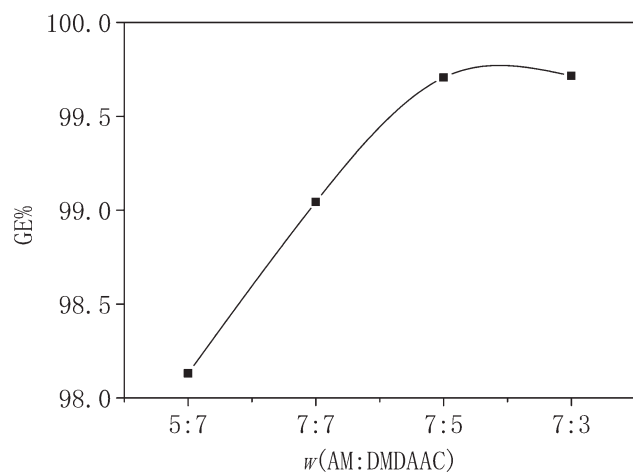


**Figure 3** The effect of monomer ratio on PG.

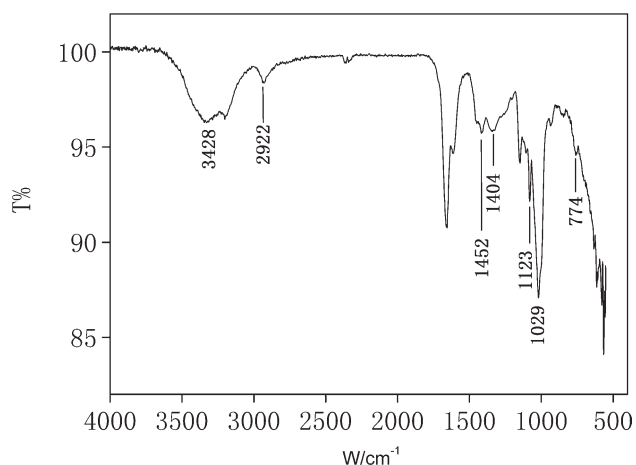
to double-methyl and methylene, which is connected to the N<sup>+</sup> of DMDAAC structural units, which is a strong evidence of incorporation of a cationic moiety onto the backbone of the starch.

### TG analysis

TGA curves of starch, CPAM and St-CPAM are shown in Figure 6. It can be seen that starch has two weight loss stages. The initial weight loss stage is at 290–340°C, which is due to selective dehydration reaction. The second stage is at 340–580°C, because the depolymerization of the macromolecules takes place with the formation of  $\beta$ -(1,6) anhydro D-glucopyranose (levoglucosan), 2-furaldehyde (furfural), and a range of lower molecular-weight volatile and gaseous fragmentation products.<sup>11</sup> The starting decomposition temperature of starch is 290°C. CPAM weight loss involves three stages at 190–260°C, 260–300°C, and 300–680°C. The first weight loss stage is due to the deamination reaction. The



**Figure 4** The effect of monomer ratio on EG.

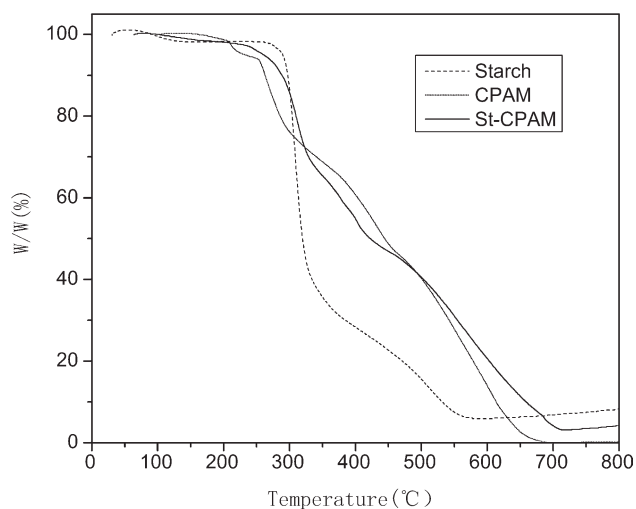


**Figure 5** FTIR spectrum of St-g-CPAM.

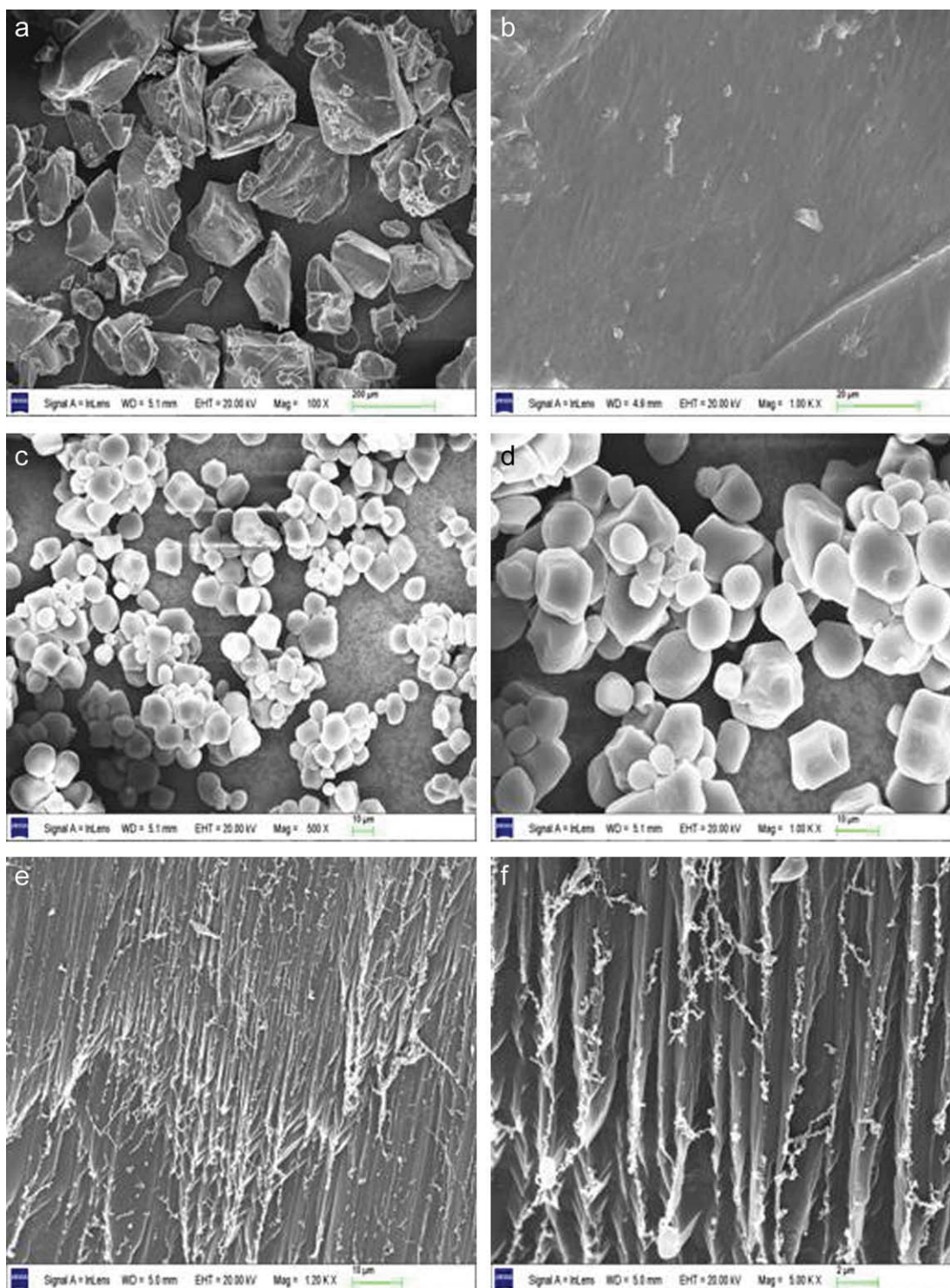
second and third weight loss stages are due to the degradation of CPAM chains. The starting decomposition temperature of CPAM is 190°C. St-g-CPAM has only one distinct weight loss stage at 250–700°C with a starting decomposition temperature of 250°C. So, the introduction of starch can improve the thermal stability of CPAM.

### SEM analysis

SEM photos of AM, starch, and St-g-CPAM are given in Figure 7. It can be seen that the specific surface of AM is smooth and angular, like some bulk crystal. The starch is oval or round, which connects with each other closely. Unlike the crystal shape of AM and oval shape of starch, a lot of branched chains of AM grafting can be observed on the surface of starch, which can increase the surface area of the starch and enhance the adsorption capacity of St-g-CPAM on the suspensions.



**Figure 6** TGA curves of starch, CPAM, and St-CPAM.

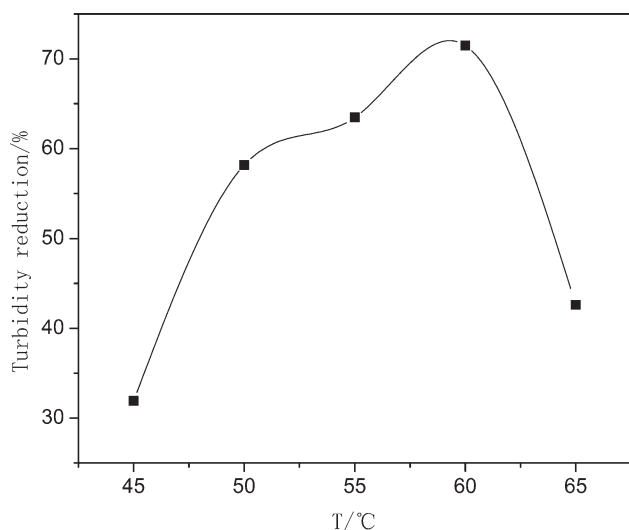


**Figure 7** SEM photos of AM, (a) AM 100, (b) AM 1000, (c) St 500, (d) St 1000, (e) St-g-CPMA 1200, and (f) St-g-CPMA 5000. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Flocculation properties

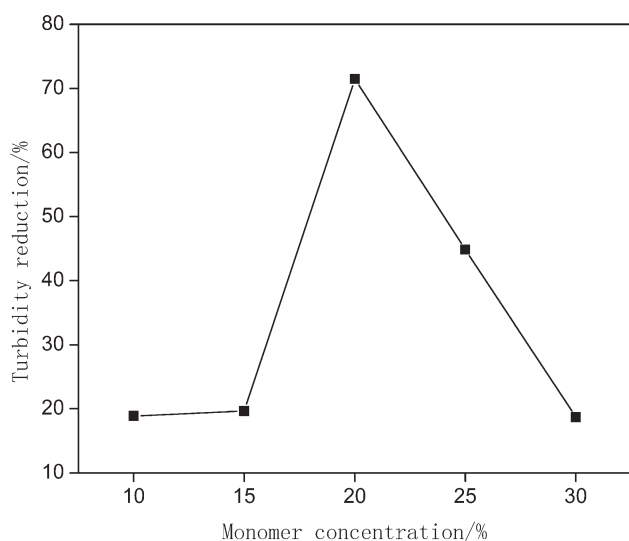
Figure 8 shows flocculating activity of St-g-CPAM prepared at different reaction temperatures. The flocculation ability of St-g-CPAM increases with the reaction temperature from 45 to 60°C; however, it

drops significantly at 65°C. When the reaction temperature increases, reaction efficiency is enhanced, the crosslinking degree together with the molecular weight of St-g-CPAM increases, which can promote the flocculation properties of St-g-CPAM. The



**Figure 8** Turbidity reduction of St-g-CPMA at various temperatures.

decreased flocculating activity at higher temperature could be explained as follows: as polymer flocculants, macromolecule configurations, and lengths play important roles in bridging flocculation. When the long-chain polymer molecules are adsorbed on the particles' surface, they tend to form loops and extend some distance from the particle surface into the aqueous phase. Their ends also dangle and get adsorbed on the surface of another particle, forming a bridge among the particles and bridging flocculation occurs.<sup>12,13</sup> However, these kind of bridges could be broken at a high temperature, which reduces the flocculating activity.<sup>14,15</sup>



**Figure 9** Effect of monomer concentration on turbidity reduction.

The flocculating activity at various monomer concentrations is shown in Figure 9. It shows that the flocculating activity increases sharply from 15 to 20%. The molecular weight of St-g-CPAM with the monomer concentration could enhance the bridging capability and, hence, improve the flocculating activity. However, when the monomer concentration is more than 20%, the molecular weight becomes excessive, which makes the flocculant more difficult to be dissolved in water, hence decrease movements of the molecular chains and function groups, and, therefore, the flocculating activity declines.

## CONCLUSIONS

St-g-CPAM can be synthesized by AM, DMDAAC, and starch with only one-step reaction. The PG and GE of the St-g-CPAM are affected by temperature, total monomer concentration, the ratio of AM and DMDAAC, and the initiator concentration. The PG and GE of St-g-CPAM can reach 92.5% and 99.7%, respectively, under optimal conditions. However, the dissolution velocity of St-g-CPAM is not ideal. Further work has been undertaken in our laboratory to acquire St-g-CPAM with a better solubility.

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